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EXPERIENCE IN THE USE OF BASICITY INDICATORS TO ESTIMATE THE REDOX POTENTIAL OF THE GLASS MELT IN CONTINUOUS PRODUCTION (A REVIEW)

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A comparative analysis of criteria of basicity (acidity) of silicate glass is performed. Examples of evaluation of the oxidizing potential of melts using the concept of acid-base relationships are analyzed with respect to the conditions of large-scale continuous sheet glass production.

One of the topical applied problems in glass production technologies is achieving an optimum redox potential (ROP) in a glass melt (optimum basicity and acidity) in tank furnaces. Solving this problem opens vast possibilities of improving glass quality, optimizing the glass-melting process, extending the service life of the glass-melting furnaces, and improving the technical and economic parameters of their performance [1, 2]. Consequently, the selection of a parameter that could be used to evaluate the ROP of glass in continuous technological processes is of great practical significance.

There is as yet no single generally accepted criterion for evaluating the basicity of silicate melts, which, in our opinion, is related to the variety of existing glass compositions, their multiple components, and chemical reactions between the components. However, the information available in the technical literature allows for an attempt to generalize the proposed basicity indicators and make a preliminary estimate of the possibility of their application in continuous production of clear silicate glass for construction and engineering purposes.

The experimental and theoretical data accumulated indicate that in the analysis of curves of chemical composition versus technological properties (viscosity, fusibility, etc.) it is advisable to use the concept of acid-base relationships [3] applying the notions of acidity and basicity.

The concept of acid-base properties of materials has evolved for more than 300 years. Despite the long history of studying the acid-base processes of materials, the authors in [4] maintain that no general definitions of “an acid” and “a base” have been developed. At the same time, the well-known theories describing the acid-base reactions make it possible to reliably predict the acid-base interaction for certain classes of chemical compounds [4].

The theories put forward to explain the acid-base reactions in melts are much less numerous. Note that the notion of “basicity (acidity”) is commonly used to describe various phenomena (formation of crystalline phases, solubility of gases in melts, evaluation of the direction of the redox reactions, etc.) in various interdisciplinary sciences (geochemistry, metallurgy) and in the technology of stone casting and ceramics [5 – 8].

It is known that the basicity of oxide silicate systems is usually characterized by the ratio between the concentrations of the base (alkali and alkaline-earth) and acid oxides. Since glass is a complex chemical compound, it is convenient to regard the basicity in glass as an additive property formed on the basis of shared participation of activities integrating a system of components.

Considering the variety of compositions used in the industry, it is clear that each group of glasses can be characterized by its own criterion taking into account the nature of their components, their structural specifics, and production conditions.

In our opinion, the parameters of basicity proposed in the technical literature can be divided into two large groups (Table 1): estimated reference parameters (hereafter “reference parameters”) and indicator parameters. The first group, owing to the absence of reliable experimental data on the activity of silicate system components, for simplification purpose is characterized by numerical values of the ratio of the concentrations of the main components in the silicate system. The simplest methods of estimating the basicity of glass involve an elementary comparison of the concentrations of alkaline and acid oxides. The parameters can be also obtained by mutual division of the concentrations of the acid and base

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TABLE 1

No.	Basicity parameter	Notations	Application area	Published source
		Estimated reference basicity parameters		
1	$K_{bas} = \Sigma R_nO_m / \Sigma Me_nO_m$	ΣR_nO_m and ΣMe_nO_m are the total weight or molar content of acid and base oxides, respectively	Metallurgy, stone casting	[8]
2	$M_{bas} = \Sigma Me_nO_m / \Sigma R_nO_m$ $M_o = (x_{Na_2O} + x_{CaO})/x_{SiO_2}$	$x_{Me_nO_m}$ is the molar part of the component (Na_2O, CaO, SiO_2)	Glass	[9]
3	$K_i = \dfrac{2(iMe_2O / iCaO \cdot N_{Me_2O}) + \sum(iMeO / iCaO \cdot N_{MeO})}{\sum(iSiO_2 / iMe_nO_m \cdot N_{Me_nO_m})}$	i and N are, respectively, the ionicity of the bond and the component content	Geochemistry	[10]
4	$K_{bas} = \dfrac{4.6x_1 + 4.7(x_2 - x_1)}{0.82x_3 + x_4 - x_2 - x_1}$	x_1, x_2, x_3, and x_4 are, respectively, the molar content of Al_2O_3, Na_2O, SiO_2, and B_2O_3	Technology of borosilicate glasses	[11]
5	$\alpha = \dfrac{2q}{m + 3n}$	q is the number of oxygen atoms bonded with SiO_2 m and n — are the numbers of oxygen atoms bonded with base oxides	Geology	[12]
6	$R = O/Si$	R is the oxygen O to Si ratio, respectively, the number of atoms of oxygen and silicon	Glass	[13]
7	$K_p = \Sigma O/\Sigma Me$	K_p is the oxygen potential ΣO and ΣMe are, respectively, the sums of oxygen ions and the metallic elements	The same	[14]
8	$K_{a.s} = \dfrac{J_{O^{2-}}}{J_{Si^{4+}} + \frac{3}{4}J_{Al^{3+}}}$	$K_{a.s}$ is the coefficient of the anion structure $J_{O^{2-}}$, $J_{Si^{4+}}$, $J_{Al^{3+}}$ are the numbers of atoms of oxygen, silicon, and aluminum, respectively	Stone casting	[15]
		Indicator basicity parameters		
9	FeO/Fe_2O_3 Fe(II)/Fe(III) Fe_2O_3/FeO	FeO, Fe(II) is the weight or molar content of the reduced form of iron, % Fe_2O_3, Fe(III) is the weight or molar content of the oxidized form of iron, %	Glass	[16, 17]
10	$d_{Fe(II)} = Fe(II) \times 100/[Fe(III) + Fe(III)]$	$d_{Fe(II)}$ is the part of the reduced form of iron	The same	[1, 2, 16]
11	$\gamma = Fe(III)/[Fe(II) + Fe(III)]$	γ is the part of the oxidized form of iron	″	[6]

oxides, or vice versa (Table 1, expressions 1 and 2). These methods are convenient, since they are easy to perform in industrial conditions. Some researchers introduce certain coefficients in such equations, taking into account the active concentrations of the system components (expression 3) [8 – 10]. There is also a number of parameters correlating the acid-base properties with the presence of structural groups in glass (expression 4) and with the state of oxygen contained in their structure (expressions 5 – 8) [11 – 15].

It is evident that the above reference parameters do not take into account the real glass-melting conditions [1, 2, 17]. The most significant factors are, first, the presence of external (not accounted for) factors producing variations in the ROP of the melt (fluctuations of the chemical or granulometric composition of the material, fluctuations in the fuel composition, fuel combustion heat, etc.); second, the presence of impurities in glass, the most common of which are iron oxides. The practice shows that these chemical compounds can have a perceptible influence on the course of the glass-melting process [2, 17].

For an indirect estimate of the glass melt ROP, an indicator basicity parameter has been proposed [1, 2], which reflects the content of the bivalent iron in glass:

$$d_{Fe(II)} = \frac{Fe(II)}{Fe(II) + Fe(III)} \times 100,$$

where $d_{Fe(II)}$ is the part of bivalent iron in glass, %; Fe(II) and Fe(III) are the weight contents of FeO and Fe_2O_3 in glass converted to metal, %.

The application of this parameter as an indicator of basicity variation is based on understanding of the behavior of iron in silicate melts. Upon introduction into a melt, the iron starts reacting with the melt according to the scheme [16]

$$2O^{2-} + 4Fe^{3+} = 4Fe^{2+} + O_2. \quad (1)$$

The ratio of the oxidized iron form Fe^{3+} to the reduced form Fe^{2+} can vary within a wide range and depends on the conditions of the process (the temperature-gas regime of

glass melting, the ROP of the batch, and the chemical composition of glass) [16].

However, the majority of authors at best consider the effect of only one of the above technological parameters. The remaining factors, as a rule, are conventionally taken as invariable. This does not correspond to the actual technology of a continuous process. Under the conditions of a large-scale production volume, a number of factors affect the glass melt and create a particular ratio between the oxidized and the reduced forms of iron in a particular glass melt. The predominant role in this processes is played by the composition of glass, whose main components create a medium in which the redox reactions between the variable-valence elements proceed.

According to contemporary concepts [3, 6, 18], such medium representing an alkaline silicate melt mainly consists of silicon-oxygen and aluminum-oxygen anions of different degrees of complexity, cations of alkali and alkaline-earth metals, and oxygen ions. The latter are categorized [18] as bridge ions (bonded in spatial structures only with silicon cations), nonbridge oxygen ions (bonded with silicon and metal cations), and free O^{2-}. From the point of view of the general theory of acids and bases [6, 18], the latter have the highest activity and represent a typical base. They are formed both in silicate formation and in thermal dissociation of silicates [18] according to the following scheme (for two-component systems):

$$MeO \cdot SiO_2 \leftrightarrow MeO + mSiO_2 \leftrightarrow Me^{2+} + O^{2-} + mSiO_2 . \quad (2)$$

Free oxygen anions O^{2-} in oxide systems are capable of acting as electron couple donors [18] similar to the role of OH^- hydroxide anions in aqueous electrolyte solutions.

Consequently, the common anion both in the acid-base and in the redox processes in multicomponent melts is the free oxygen anion O^{2-} (reactions (1) and (2)). A result of the reaction of iron with O^{2-} anions present in the melt is the respective modification of the concentrations of bi- and trivalent iron in glass. An increase in the content of bivalent iron indicates a decrease in the concentration of free oxygen anion O^{2-} and, accordingly, an increase in the acidity of the glass melt (a decrease in the melt ROP). On the other hand, an increase in the content of iron in the higher valence state reflects an increase in the oxidizing potential (basicity) of the glass. Note that any external and internal factors in the process finally produce a modification of the concentration of free oxygen anions and, accordingly, a modification of the oxidation state of the glass melt.

The indicator parameter of glass basicity proposed by us [1, 2] and other expressions similar in meaning are referred to the second group of the ROP parameters (Table 1, expressions 9 – 11). The methods for the calculation of the parameters in this group are equivalent, since the sum of the concentrations of bi- and trivalent iron in each specific composition is invariable.

It is interesting to carry out a comparative analysis of the variations of the melt ROP in the real conditions of an operating glass-melting furnace using the most typical ratios from the reference parameter group (the basicity modulus, Table 1, expression 2):

$$M_{bas} = (Na_2O + CaO + MgO)/(SiO_2 + Al_2O_3),$$

where the oxide content is expressed in wt.%, and the indicator basicity parameter proposed in [1, 2] (the second group of criteria of the glass ROP; Table 1, expression 10).

Nine technological processes were carried out in continuous regenerative gas-heated tank furnaces of similar designs. The design specifics of the glass-melting furnaces are described in detail in [2, 19]. The chemical composition of glasses, their main process parameters, and the melting and working characteristics are given in Table 2. Technological processes 1A and 2A in furnaces Nos. 1 and 2 were performed using a concentrated material and additional effective clarifiers; in processes 1B and 2B the concentrated material was replaced by the traditional batch materials with a higher content of ferric oxide. New types of materials were used in processes 1C and 2C; in particular, process 2C was based exclusively on cullet as the initial material [19]. Note that the chemical composition of glass in process 2B was corrected by decreasing the concentration of high-melting oxides and increasing the flux content. In processes 3A, 3B, and 3C in furnace No. 3 using the traditional materials, the reference glass composition as well was replaced by a lower-melting composition [20]. In process 3C, a melting catalyst Na_2SiF_6 was introduced to increase the process efficiency.

An analysis of the performance of the glass-melting furnaces revealed the following general principles. A modification of the type of materials in each case was accompanied by an increase in the trivalent iron content in the glass: from 0.0535 to 0.180% (3.6 times) in furnace No. 1 and 4.3 times (from 0.041 to 0.178%) in furnace No. 2. The fluctuations in the Fe_2O_3 content in furnace No. 3 were within the limits corresponding to the technological regulations (0.06 – 0.07%).

The reference basicity parameter M_{bas} in furnaces No. 2 and 3 increased on the average from 0.337 to 0.350 when the composition was replaced by a higher-melting one. The chemical compositions in processes 2B, 2C, 3B, and 3C in their degree of fusibility corresponded to the glass produced in furnace No. 1 ($M_{bas} = 0.350 \pm 0.002$). At the same time, transition to new types of material (furnace No. 1) and increased flux concentration in the glass (furnaces Nos. 2 and 3), contrary to the expectations, lowered the glass melt homogeneity [2] and required a higher maximum melting temperature.

All this indicates an insufficient correlation of the reference parameter M_{bas} with the actual variations in the ROP of the melt in a continuous process. The latter is due to the fact that a number of factors in the processes considered simultaneously affect the actual basicity of the melt and the state of

TABLE 2

Parameter	Technological process								
	furnace No. 1			furnace No. 2			furnace No. 3		
	1A	1B	1C	2A	2B	2C	3A	3B	3C
Design capacity, tons/day	160	160	160	75	75	75	140	140	140
Batch component:									
raw material	Concentrated	Traditional	Local	Concentrated	Traditional	None	Traditional		
with addition of:									
clarifiers	Present	Absent	Present	Absent					
catalysts	Absent								Present
cullet (wt.%)	30	30	30	30	30	100	30	30	30
Content in glass, wt.%, from analysis:									
$SiO_2 + Al_2O_3$	77.62	73.60	73.80	74.55	73.77	73.44	74.63	73.30	73.43
$Me_2O + MeO$	25.87	25.93	25.71	24.48	25.66	25.87	24.38	26.02	25.79
$M_{bas} = \frac{Na_2O + CaO + MgO}{SiO_2 + Al_2O_3}$	0.351	0.352	0.348	0.328	0.348	0.352	0.327	0.355	0.351
ROP of batch [16]	15.80	15.48	13.17	18.86	116.80	–	11.72	9.09	16.27
Content of CO in atmosphere, vol.%	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0
Weight content, %:									
$Fe_2O_3 + FeO$	0.0535	0.0730	0.1800	0.0410	0.1180	0.1780	0.0600	0.0710	0.0610
Fe(II)	0.0060	0.0171	0.0481	0.0055	0.0250	0.0380	0.0124	0.0179	0.0210
$d_{Fe(II)} = \frac{Fe(II)}{Fe(II) + Fe(III)} \times 100$, %	16.0	33.5	38.1	19.1	30.1	40.0	25.9	37.5	48.8
Diathermancy index [20]	Not determ.	6.9	5.7	Not determ.	6.7	5.6	Not determ.		
Glass homegeneity, °C	1.1 – 1.3	1.1 – 1.3	1.8	1.1 – 1.3	1.1 – 1.3	2.5 – 3.0	1.5 – 2.0	1.5 – 2.0	1.5 – 2.0
Melting temperature, °C	1520	1520	1560	1470	1500	1520	1470	1510	1500

equilibrium of the variable-valence forms of iron. In furnace No. 3 these factors acted only in one direction. A decrease in the ROP of the batch (the chemical composition of glass being constant), an increase in the iron content in the glass, and an increased maximum melting temperature (Table 2) led to growth in the concentration of bivalent iron and an actual increase in the reducing potential of the glass (a decrease in its basicity), which was manifested through an increased share of the reduced form of iron $d_{Fe(II)}$ from 16% (process 1A) to 38.1% (process 1C).

The effect of a number of oppositely directed factors on the melt was observed in the two latter cases (furnaces Nos. 2 and 3). On the one hand, a modification in the concentration of the main glass components towards an increasing flux content should produce a growth in the basicity of glass (transition of processes from 2A to 2B, from 3A to 3B), and, on the other hand, a decrease in the batch ROP is capable of increasing the reducing potential (acidity) of the glass melt. A simultaneous increase in the Fe_2O_3 concentration (and, accordingly, FeO) in the melt and an increased melting temperature as well should facilitate an increase in the melt acidity. In fact, the share of the reduced iron form $d_{Fe(II)}$ in the glass produced in furnaces Nos. 2 and 3 after modifying the process parameters increased, which is a manifestation of an actual decrease in the melt basicity.

The developed criterion (an indicator parameter of glass basicity $d_{Fe(II)}$) makes it possible to indirectly compare the basicity level of melts in continuous processes. For this purpose it is necessary to rank the indicator parameters of glass basicity in the considered processes in the order of variation of the Fe(II) content. Thus, the Fe(II) content is equal to (%): 48.8 in process 3C, 40.0 in 2C, 38.1 in 1C, 37.5 in 3B, 30.1 in 2B, 33.5 in 1B, 29.5 in 3A, 19.1 in 2A, and 16.0 in 1A.

An analysis of the variation of $d_{Fe(II)}$ indicates that the highest acidity is registered in the melt produced in process 3C after introducing the Na_2SiF_6 melting catalyst; then $d_{Fe(II)} = 48.8\%$. The maximum basicity is registered in the melt in process 1A produced using the concentrated material and the clarifiers. The maximum melting temperatures measured with respect to the gas medium (Table 2) satisfactorily correlate with the above ranking in the respective processes. Its highest values (1520 – 1560°C) are registered in processes 1C and 2C in melting glasses with an increased acidity level ($d_{Fe(II)}$ is equal, respectively, to 38.1 and 40.1%). The lowest values (1470°C) are observed in processes 2A and 3A with an enhanced level of basicity. The melt produced in process 3C ($d_{Fe(II)} = 48.8\%$) with the Na_2SiF_6 additive should be considered separately. Under a relative low melting temperature equal to 1500°C this melt has the lowest basicity values among the considered melts.

The practical testing of the glass basicity indicator occurred during the start-up of a mini-system for producing polished float glass [1] and demonstrated its efficiency in optimizing the technological process.

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